



# Halo-organic pollutants: The effect of an electrical bias on their decomposition mechanism on porous iron electrodes

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## ABSTRACT

The de-halogenation processes of  $\text{CH}_2\text{BrCHBrCOO}^-$  and of  $\text{CH}_2\text{ClCH(OH)COO}^-$  on Zero Valent Iron (ZVI) powders and porous iron electrodes were studied. The results suggest that by applying a negative voltage bias on the electrode, the composition of the products obtained is dramatically changed. Furthermore, the applied potential inhibits the passivation of the ZVI. Thus, it is recommended that the application of a negative potential to porous ZVI is desirable in batch treatment of halo-organic pollutants.

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## 1. Introduction

Halo-organic compounds are major environmental pollutants [1]. The halogen substituents can increase the hydrophobicity of organic compounds, increasing their tendency to become bio-accumulated in the food chain as well as absorbed by soil. See for example the following recent reviews (references [1–9]). Pollution caused by anthropogenic halogenated organic compounds is a serious environmental problem for decades [10–13]. Most of the top hundred species in the List of Hazardous Compounds [14] are halogenated compounds (including chlorinated and brominated organic compounds) [15,16]. Large quantities of chlorinated organic molecules cause environmental pollution as a result of their widespread use as herbicides, insecticides, fungicides, solvents, hydraulic and heat-transfer fluids, plasticizers, cleaning agents, fumigants, aerosol propellants, gasoline additives, degreasers and intermediates for chemical syntheses [17].

De-halogenation reactions are involved in synthetic chemistry [18,19] and in the decomposition reactions of halogenated pol-

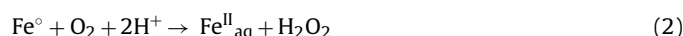
lutants [20–27]. Halo-organic compounds, mainly chloro- and bromo-organic, are produced in large scale as solvents, pesticides, raw materials for organic synthesis and flame-retardants [28]. Hence, the importance of the research on the reduction mechanisms of these compounds and the substitution of the halogen atoms by less harmful substituents.

Zero Valent Iron (ZVI) is one of the most efficient de-halogenation agents and is widely used both in treating polluted underground water streams and in industrial batch processes. See for example the following recent reviews [29–36]. ZVI has been known for its hazardous waste removal ability since the seminal works of Gillham and O'Hannesin [29] as well as Matheson and Tratnyek in 1994 [30]. Two mechanisms are involved in the de-halogenation processes induced by ZVI:

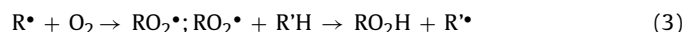
I. Direct dehalogenation:



II. Via oxidation of the organic substrate in a mechanism involving the Fenton reaction [34,35]:



Followed by the reaction of  $\text{Fe}^{\text{II}}_{\text{aq}}$  with  $\text{H}_2\text{O}_2$  or with other peroxides formed in the process, e.g. via:

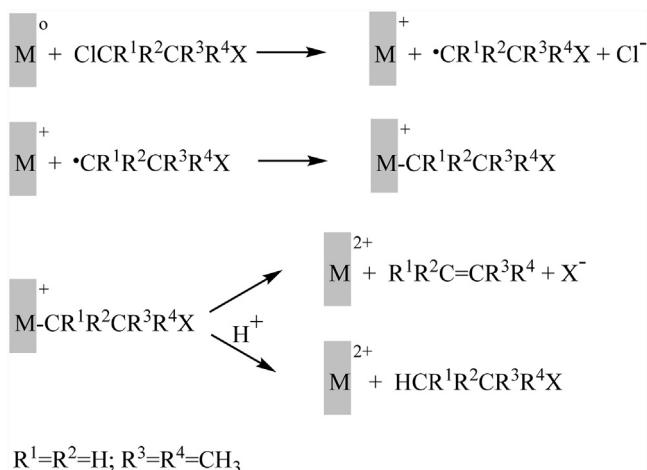


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**Scheme 1.** Mechanism for the de-halogenation of halo-organic compounds, good leaving groups (X), on the  $\beta$  position, on metal surfaces [42]. Adapted with permission from Ref. [42]. Copyright (2006) American Chemical Society.

It is commonly assumed that  $\text{OH}^{\bullet}$  radicals are formed in the Fenton and Fenton like reactions. However, recent results, mainly in non-acidic solutions, point out that this is not always the case [37–41].

On the other hand, the application of ZVI has several drawbacks as listed in the review by Dong *et al.* [36]:

- The surface area of permeable iron membranes is relatively small, a difficulty that can be overcome using  $\text{Fe}^{\circ}$ -nano-particles.
- The surface of ZVI is covered by  $\text{Fe}^{\text{III/II}}$ -hydroxides/oxides due to corrosion. This cover increases due to the reduction of the pollutants.
- Due to the formation of  $\text{Fe}^{\text{III/II}}$ -hydroxides/oxides the application of ZVI is preferable in slightly acidic solutions. However, in practice work in neutral solutions is needed.

The metal-surface de-halogenation mechanism of some halo-organic compounds, containing good leaving groups on the  $\beta$  position to the halogen substituent (in which the formation of the following radicals is expected:  $\bullet\text{CH}_2\text{CH}_2\text{NH}_3^{+}$ ,  $\bullet\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$ ,  $\bullet\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$  and  $\bullet\text{CH}_2\text{CH}_2\text{OH}$ ) was studied [42]. The metal powders investigated were  $\text{Ni}^{\circ}$ ,  $\text{Co}^{\circ}$  and  $\text{Fe}^{\circ}$ . The results indicated that the mechanism of these de-halogenations is as follows in Scheme 1 [42]:

(Note: the metal particles consist of  $\text{M}^{\circ}$  atoms, the charge on the particle is a charge delocalized on the entire particle or on one atom on the surface. Hence, it appears in the text as  $(\text{M}^{\circ})^{2+/+}\text{-R}$ ).

The first reaction in this scheme suggests that the radicals,  $\text{R}^{\bullet}$ , are the first short-lived intermediates formed in the de-halogenation processes. As these radicals are formed in the vicinity of the metal surface and as the reactions of radicals with metals are very fast [43–48], the second reaction is clearly an essential part of the de-halogenation process. These reactions have very high rate constants, probably due to the fact that the electrons in the conduction band behave as radicals and react therefore with other radicals [49]. The properties of the transients  $(\text{M}^{\circ})^{+}\text{-CR}^1\text{R}^2\text{CR}^3\text{R}^4\text{X}$  formed in the second reaction in the scheme depend on the nature of M and on the nature of the substituents  $\text{R}^1$  and X [42]. The mechanisms of decomposition of the  $(\text{M}^{\circ})^{+}\text{-CR}^1\text{R}^2\text{CR}^3\text{R}^4\text{X}$  transients depend also on the pH of the aqueous medium, on the temperature and probably on the nature and concentration of plausible substrates present in the medium. The transients  $(\text{M}^{\circ})^{+}\text{-CR}^1\text{R}^2\text{CR}^3\text{R}^4\text{X}$  might in principle decompose also *via* homolytic decomposition of the M–C bond and/or *via* reaction with substrates present in the medium.

However, the latter reactions were as of yet not reported. The characteristics of the substrate molecule and reaction conditions will determine the main products of the de-halogenation process.

In many organic-electrochemical processes transient radicals and radical-ions are formed. For example, during oxidation of  $\text{RCO}_2^{-}$  in the Kolbe reaction [50–52], the primary radical  $\text{RCO}_2^{\bullet}$  decomposes into  $\text{R}^{\bullet} + \text{CO}_2$  and the nature of the final products is the result of reactions of the  $\text{R}^{\bullet}$  radicals. As radical formation in electrochemical reactions occurs in the vicinity of the electrode, they often react with the electrode [53–58]. The mechanisms of decomposition of the transients thus formed often depend on the potential applied in the electrochemical process [53,59].

Thus for example the mechanism of the electrochemical de-halogenation of 1,4-dibromobutane in dimethylformamide (DMF) depends on the applied cathodic potential [50]. The products mixture obtained may only be explained in terms of a transient consisting of a radical bound to the metallic electrode. Reduction of diazonium salts on electrode surfaces produces either an intermediate or a stable product with a covalent bond between an organic residue and the metallic electrode [55,60–63]. Similar reactions were observed on conductor and semi-conductor surfaces [54,61,64–66]. Also, the initiation stage in the production of organo-metallic compounds through electrochemical reactions with metals such as Pd, Cd and Hg involves the formation of transients with M–C  $\sigma$  bonds [56]. The formation of  $\sigma$  bonds between radicals and other metal surfaces as well as semi-conductors and metal oxides surfaces was also reported [43–49,67–72].

It was reported that the reduction of  $\text{CCl}_4$  on an iron electrode surface, under an electrical bias, yields  $\text{CH}_4$  and that no intermediates, e.g.  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$  or  $\text{CH}_3\text{Cl}$ , are observed [20]. On the other hand, it was reported that the reduction of  $\text{CHCl}_3$  on an iron surface electrode occurs at a slower rate compared to  $\text{CCl}_4$  [73,74]. The latter observation is in accord with the report that the de-chlorination of  $\text{CCl}_4$  with iron powder does not produce  $\text{CH}_4$  [67]. This apparent discrepancy was clarified by the report that the products of de-halogenation of  $\text{CCl}_3\text{CO}_2^{-}$  on a porous iron electrode depend on the negative voltage bias applied on the electrode [59].

Thus, applying a constant electrical bias on a metallic electrode at potentials that do not induce faradaic currents may affect the cleavage mechanisms of the transients having metal-carbon  $\sigma$  bonds as well as on the final products. The applied potential bias has an additional advantage: it inhibits the formation of the  $\text{Fe}^{\text{III/II}}$ -hydroxides/oxides and thus accelerates the de-halogenation process. Therefore, it was decided to study the de-halogenation reactions of 2,3-dibromo-propionate and 2-hydroxyl-3-chloro-propionate on an iron powder surface at room temperature. This study focused on: (1) the de-halogenation mechanism of the halo-organic compounds performed on an iron powder surface and on porous iron electrodes; (2) the influence of the electrical bias applied on porous electrodes on the efficiency of the de-halogenation processes and on their mechanisms. Understanding these mechanisms may contribute to the development of new and efficient de-halogenation processes.

## 2. Experimental section

### 2.1. Materials

All chemicals used were of analytical purity level and purchased from Sigma-Aldrich, Merck, J.T. Baker and Frutarom. Iron powder, particle size  $\leq 10 \mu\text{m}$  and 99% purity, was purchased from Merck. The water used was de-ionized and further purified by a Millipore Milli-Q system, achieving a final resistance of  $>15 \text{ M}\Omega \text{ cm}$ . The inorganic gases were of analytical purity level and purchased from

Maxima. Measurements of pH were carried out with a Microprocessor Hi 9017 pH meter, from Hanna instruments.

## 2.2. Iron powder activation

The iron powder was activated before each experiment by washing 10 g metal powder with a 0.1 M  $\text{H}_2\text{SO}_4$  solution, for a period of 2 min. Then the powder was washed 8 times with 8 mL distilled water. This procedure removes oxides from the surface.

## 2.3. Electrochemical analysis

Electrochemical measurements of de-aerated solutions were performed with a potentiostat/galvanostat, model 263 A from EG&G. A 100 mL glass-working cell from Metrohm, with 3 independent electrodes, was used: a porous iron surface electrode (as the working electrode), a 0.222 V (vs. NHE) calomel reference electrode and a platinum wire counter electrode. All the yields given in this paper are the average of at least three independent experiments.

## 2.4. Preparation of porous surface iron electrode

The electrode was prepared according to the thermal baking method. For that purpose, a 10  $\mu\text{m}$  particle size iron powder from Merck was mixed with boric acid powder in an 8:1 ratio. Distilled water was then added until a dark gray dense mixture was obtained. A 1 mm thick iron rod was then coated with this mixture until reaching 3 mm thickness and was introduced in vertical position into a previously heated oven at 550 °C, under argon gas flow. The resistivity (between the rod and the coating) of the resulting electrode was determined. When a resistivity higher than 0.2  $\Omega$  was observed, the electrode was immersed into a 10% hydrochloric acid solution for 5 min, washed with distilled water and dried. The electrode thus obtained had a resistivity lower than 0.2  $\Omega$ .

## 2.5. Ion chromatography

Bromide ( $\text{Br}^-$ ) concentrations were determined by an ion chromatograph from Jasco, model PU-980 Intelligent, equipped with a Hamilton-PRP-X100 column (250  $\times$  4.1 mm<sup>2</sup>) and a conductivity detector. The mobile phase was 4 mM  $\text{H}_5\text{C}_6\text{CO}_2\text{Na}$  at a flow of 2.5 mL/min. Chloride ( $\text{Cl}^-$ ) concentrations were determined by reacting the sample with a  $\text{Fe(III)nitrate}/\text{Hg(II)(NCS)}_2$  reagent and measuring the developed color using a UV–vis spectrophotometer at  $\lambda = 460$  nm. The organic acids analyses were performed according to a new combined method of HPLC and liquid ion chromatography which was developed for the determination of short organic acids [75,76]. HPLC reversed-phase separation, anion suppression, and conductivity detection were employed for that purpose. A Dionex, model DX-500 ion chromatograph, equipped with an Ion exclusion type suppressor, a conductivity detector and an OA Acclaim column was used. A 2.5 mM methyl sulfonic acid at a flow of 0.7 mL/min was the mobile phase used [76].

## 3. Results and discussion

### 3.1. The de-halogenation of $\text{CH}_2\text{BrCHBrCOO}^-$

When  $\text{CH}_2\text{BrCHBrCOO}^-$  (note that the  $\text{pK}_a$  of  $\text{CH}_3\text{CHBrCO}_2\text{H}$  is 3.0, therefore in the solutions at pH 3.0 there is always a mixture of the acid and its conjugated base; for short in the manuscript always the conjugate base is used) is introduced to a suspension of iron activated powder, a relatively fast and complete de-bromination of  $\text{CH}_2\text{BrCHBrCOO}^-$  is achieved as described in Fig. 1.

The results in Fig. 1 point out that  $\text{Br}^-$  ions are readily released from the molecule. In the case of  $\text{CH}_2\text{ClCHClCOO}^-$ , the pro-

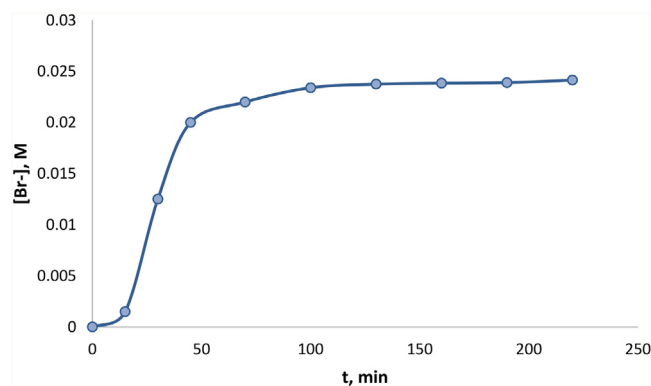


Fig. 1.  $\text{Fe}^0$  powder  $\text{CH}_2\text{BrCHBrCOO}^-$  de-bromination product ( $\text{Br}^-$ ) concentration vs. time. 10 g activated iron powder in 2.5 mL Ar-saturated aqueous solution at pH 3.0,  $T = 25^\circ\text{C}$  containing 0.012 M  $\text{CH}_2\text{BrCHBrCOO}^-$ .

cess is considerably slower and incomplete de-chlorination is obtained [75]. When higher concentrations of  $\text{CH}_2\text{BrCHBrCOO}^-$  were treated using the activated iron powder, the yield of  $\text{Br}^-$  ions increased after four hours, but in a non-linear pattern. A four-fold concentration of the substrate causes a maximum twofold increase of the  $\text{Br}^-$  concentration. This occurs due to the relatively small available active surface of the iron powder, caused by the passivation processes due to the formation of  $\text{Fe}^{\text{III/II}}$ -hydroxides/oxides on the iron thus slowing the de-halogenation process. The  $\text{CH}_2\text{BrCHBrCOO}^-$  de-bromination was also analyzed for the organic products. Table 1 sums-up the product distribution of  $\text{CH}_2\text{BrCHBrCOO}^-$  de-bromination obtained under different conditions.

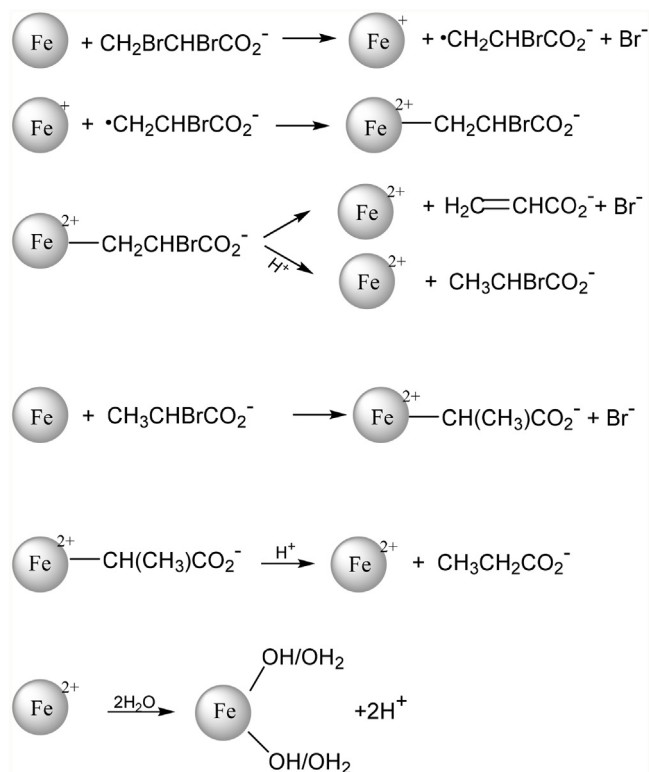
The samples contained 10 g activated iron powder in 2.5 mL Ar-saturated aqueous solution containing 0.012 M  $\text{CH}_2\text{BrCHBrCOO}^-$ , 4 h,  $T = 25^\circ\text{C}$ .

Acrylic and propionic acids are the major products of  $\text{CH}_2\text{BrCHBrCOO}^-$  de-bromination. At pH 3 acrylic acid is formed at higher yields than propionic acid with and without stirring. However, at pH 6 the yield of propionic acid is higher than that of acrylic acid. When the suspensions are stirred the product distribution is changed dramatically as the yield of acrylic acid increases at both pH 3 and pH 6. The acrylic/propionic acids ratio changes by ca. one order of magnitude upon stirring.

Scheme 2 presents the suggested mechanism for the de-bromination of  $\text{CH}_2\text{BrCHBrCOO}^-$  on activated iron powder surface, at  $25^\circ\text{C}$ , under Ar-saturated atmosphere. The formation of acrylic-acid/acrylate can only occur via the decomposition of the intermediate  $(\text{Fe}^\circ)^+ - \text{CH}_2\text{CHBrCO}_2^-$  (or  $(\text{Fe}^\circ)^+ - \text{CH}(\text{CO}_2^-)\text{CH}_2\text{Br}$ ) thus proving that the first step in the de-bromination process is the formation of a radical that reacts with the surface forming a metal-carbon  $\sigma$  bond. The formation of the radical in de-halogenation processes on  $\text{Fe}^0$  was earlier proven [42,59,67]. The detailed mechanism of this reaction can in principle be via three possibilities: a. electron transfer from the  $\text{Fe}^\circ$  to form  $\text{R-Br}^\cdot$  which decomposes later; b. electron transfer from the  $\text{Fe}^\circ$  to form directly  $\text{R}^\cdot + \text{Br}^-$ ; c. abstraction of a bromide by the  $\text{Fe}^\circ$  to form an adsorbed bromide and the  $\text{R}^\cdot$  radical. The experimental data does not enable to decide which of these mechanisms takes place. The decomposition of this  $\sigma$  bond may lead to the formation of either  $\text{CH}_3\text{CH}_2\text{COO}^-$  or  $\text{CH}_2=\text{CHCOO}^-$ . It is not clear yet whether the primary radical produced is  $^\cdot\text{CH}_2\text{CHBrCO}_2^-$ , as shown in Scheme 2, or  $^\cdot\text{CH}(\text{CH}_2\text{Br})\text{CO}_2^-$  which is thermodynamically more feasible. It should be noted that the resulting products are the same in both cases and that the de-brominated molecule is very close to the surface causing the next reactions to occur rapidly, making it difficult to detect transients. The pH effect on

**Table 1**  
Product distribution of the de-bromination of  $\text{CH}_2\text{BrCHBrCOO}^-$  on an activated iron powder.

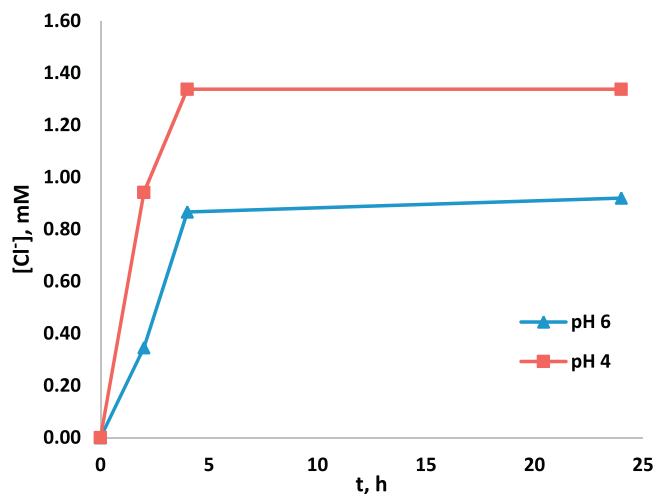
| Initial pH | Stirring | Acrylic acid, mM | Propionic acid, mM | [Acrylic acid]/[Propionic acid] |
|------------|----------|------------------|--------------------|---------------------------------|
| 3          | –        | 6.6              | 3.2                | 2.1                             |
| 3          | +        | 11.4             | 0.39               | 29                              |
| 6          | –        | 2.4              | 6.2                | 0.38                            |
| 6          | +        | 9.6              | 2.4                | 4.1                             |



**Scheme 2.** Mechanism of de-bromination of  $\text{CH}_2\text{BrCHBrCOO}^-$  on activated iron powder surfaces.

the composition of the final products seems surprising as one expects that the acid catalyzed heterolysis of the  $\text{Fe}-\text{C}$   $\sigma$  bonds is faster in acidic solutions. Note that this reaction clearly occurs also *via*:  $(\text{Fe}^\circ)^{2+}-\text{CR}^1\text{R}^2\text{R}^3 + \text{H}_2\text{O} \rightarrow (\text{Fe}^\circ)^{2+} + \text{HCR}^1\text{R}^2\text{R}^3 + \text{OH}^-$ . However, it was noted that the hydrolysis of the  $\text{Cr}^{\text{III}}-\text{C}$  bond in  $(\text{nta})(\text{H}_2\text{O})\text{Cr}^{\text{III}}-\text{CR}^1\text{R}^2\text{OH}$  increases with the pH at  $\text{pH} \geq 5.5$ . This was attributed to a  $\text{pK}_a$  of the *cis*-water molecule that stabilizes a transition state in which the attacking  $\text{H}_2\text{O}$  molecule is hydrogen bonded to the  $\text{OH}^-$  ligand [77]. Similar transition states stabilized by hydrogen bonds to the hydroxide/oxide layers formed on the surface of the porous iron at higher pHs are expected to affect analogously the kinetics of decomposition of the  $(\text{Fe}^\circ)^{2+}-\text{C}$  bond. Of special interest is the stirring effect on the composition of the final products. The stirring slows down the increase in the pH near the Fe surface, by reducing the local concentration of  $\text{OH}^-$ , thus decreasing the relative rate of the heterolysis of the  $\text{Fe}-\text{C}$  bond, thereby increasing the probability of the  $\beta$ -elimination of the second bromide resulting in the formation of acrylic acid. This effect is clearly more dramatic at pH 3.

In order to study the effect of an electrical bias application on the de-halogenation mechanism, a substrate that reacts less efficiently than  $\text{CH}_2\text{BrCHBrCOO}^-$  should be investigated. Therefore, it was decided to study the de-chlorination of  $\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-$  as the  $\text{C}-\text{Cl}$  bond is considerably stronger than the  $\text{C}-\text{Br}$  bond. First, this reaction was studied when  $\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-$  was mixed with  $\text{Fe}^\circ$  powder. The chloride yield as a function of time is summed up in



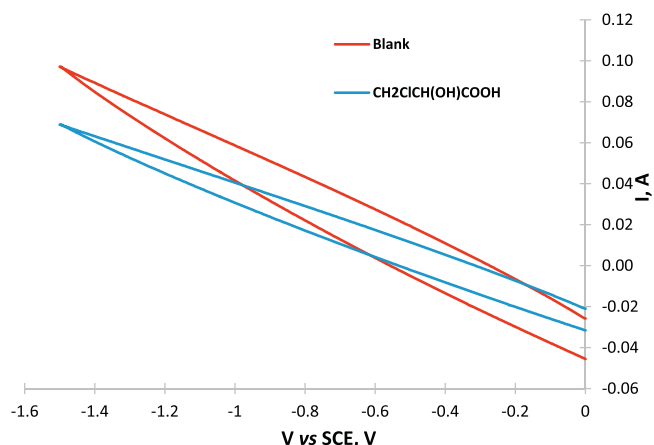
**Fig. 2.** Chloride yield as a function of time in the  $\text{Fe}^\circ$  powder catalytic de-chlorination of  $\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-$ . 10 g activated iron powder in 2.5 mL Ar-saturated aqueous solution at initial pHs of 4.0 (red line, rectangles) and 6.0 (blue line, triangles) containing 0.010 M  $\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-$ , the final pH was 7.5;  $T = 25^\circ\text{C}$ . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Fig. 2.** The results suggest that this reaction is considerably slower than the de-bromination reaction and that it does not reach completion. The observation that the reaction does not proceed after the first few hours is attributed to the passivation of the surface by the formation of the  $\text{Fe}^{\text{III/II}}$ -hydroxides/oxides cover on the  $\text{Fe}^\circ$  surface.

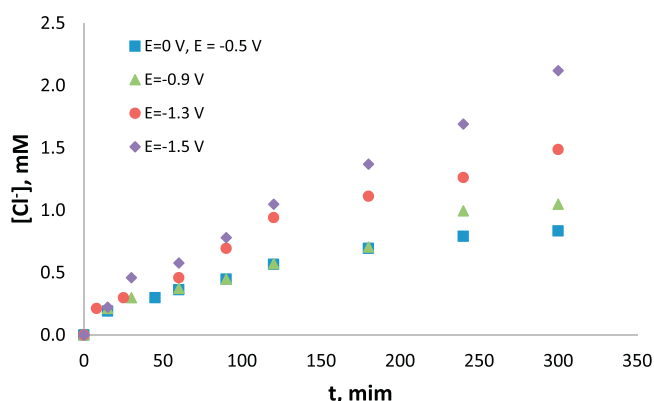
### 3.2. De-halogenation performed on a porous iron electrode under the application of an electrical bias – de-chlorination of $\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-$

The influence of voltage application on the de-halogenation process of  $\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-$  on a porous iron electrode was studied using a home-made porous iron electrode [59]. CV measurements in the voltage range of (0.0 to  $-1.5$ ) V vs. SCE show no redox process of  $\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-$  (Fig. 3). No faradaic current is observed in the presence of  $\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-$ , indicating that this substrate does not undergo electrochemical reduction on the electrode surface under these conditions between (0.0 to  $-1.5$ ) V vs. SCE.

The de-chlorination reaction of  $\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-$  was followed kinetically under different voltage biases by measuring the  $\text{Cl}^-$  concentration produced in the solution as a function of time (Fig. 4). An induction time is observed at the beginning of the reaction. This induction time probably stems from the time required to reduce the oxides/hydroxides coating on the electrode surface, as no faradaic current is observed in the CV measurements (Fig. 3). The results at zero bias fit those in Fig. 3. The larger the negative voltage bias the larger the  $\text{Cl}^-$  yield and at a bias of  $-1.5$  V the  $\text{Cl}^-$  yield becomes linear with time. These results support the hypothesis that at negative potential biases the surface  $\text{Fe}^{\text{III/II}}$  hydroxide/oxide layer is reduced and no passivation layer is formed on the electrode. Thus, the electrode surface is available for the de-halogenation reaction.



**Fig. 3.** Cyclic voltammetry of  $\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-$  performed on a porous iron electrode with a scan rate of 50 mV/s. 0.010 M  $\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-$ ; 0.10 M  $\text{NaClO}_4$  electrolyte, pH 7.0,  $\text{Fe}^\circ$  electrode ( $R=0.2\ \Omega$ ), Ar-saturated atmosphere (blue line). Blank: electrolyte 0.10 M  $\text{NaClO}_4$ , pH 7.0,  $\text{Fe}^\circ$  electrode ( $R=0.2\ \Omega$ ), Ar-saturated atmosphere (red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



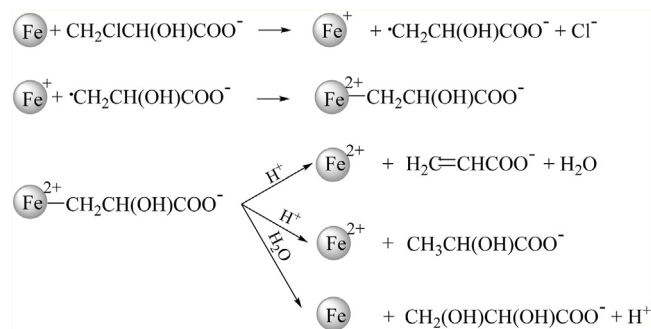
**Fig. 4.**  $\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-$  de-chlorination product ( $\text{Cl}^-$ ) concentration vs. time on a porous iron electrode ( $R=0.2\ \Omega$ ) at various potentials vs. SCE. Ar-saturated aqueous solution containing 0.010 M  $\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-$ , 0.10 M  $\text{NaClO}_4$  at initial pH of 7.0,  $T=25^\circ\text{C}$ .

**Table 2**  
Reaction products and final pH values of  $\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-$  de-chlorination.

| E, V | Acrylic acid | Lactic acid | Glyceric acid | Final pH |
|------|--------------|-------------|---------------|----------|
| −1.5 | –            | –           | +             | 3        |
| −1.3 | +            | +           | +             | 8        |
| 0    | +            | +           | –             | 11       |

The de-chlorinations were performed on a porous iron electrode, under different applied potentials for 5 h. Iron electrode ( $R=0.2\ \Omega$ ), Ar-saturated aqueous solutions containing 0.010 M  $\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-$ , 0.10 M  $\text{NaClO}_4$  at initial pH of 7,  $T=25^\circ\text{C}$ .

The final pHs in these experiments and the composition of the final products were measured and are summarized in Table 2. The results clearly support different mechanisms of decomposition of the  $(\text{Fe}^\circ)^{2+}\text{-CH}_2\text{CH}(\text{OH})\text{CO}_2^-$  transients first formed. In the absence of a potential bias, only acrylic- and lactic- acids are formed, the pH of the solution rises and the process stops at low yields. At a



**Scheme 3.** Proposed mechanisms for the de-chlorination reaction of  $\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-$ , performed on an iron electrode surface at different negative charges.

**Table 3**  
 $\text{Cl}^-$  yield from  $\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-$  de-chlorination.

| $[\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-]$ , M | $[\text{Cl}^-]$ , mM |
|---|----------------------|
| 0.010   | 2.10                 |
| 0.10  | 3.15                 |

potential of  $-1.3\ \text{V}$  a mixture of acrylic, lactic- and glyceric acids is obtained and the pH of the solution is nearly not affected. At a potential of  $-1.5\ \text{V}$  only glyceric acid is formed and the solution becomes acidic. These results are in accord with a voltage dependent competition between the reactions outlined in Scheme 3.

It should be noted that at potentials more negative than the redox potential of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ ,  $-0.44\ \text{V}$ , one expects that the  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  will be reduced by the electrode which will therefore act as an electro-catalyst.

The effect of the initial  $[\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-]$  on the  $\text{Cl}^-$  yield in the de-chlorination reaction was investigated on an electrode at  $-1.5\ \text{V}$ . A tenfold increase of the initial  $[\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-]$  resulted in a 1.5 fold increase in the  $\text{Cl}^-$  yield after a five hours reaction on an electrode at  $-1.5\ \text{V}$  vs. SCE. This non-linear dependence on the substrate initial concentration stems probably from the rate of decomposition of the  $(\text{Fe}^\circ)^{2+}\text{-CH}_2\text{CH}(\text{OH})\text{CO}_2^-$  intermediate. If the decomposition of this intermediate is the reaction's rate determining step, the increase in the  $\text{Cl}^-$  yield is not expected to be linear with the substrate concentration, as shown in Table 3. It was also found that  $\text{Cl}^-$  yield increases with temperature, indicating that the temperature affects the de-chlorination reaction kinetics. Alternatively, the de-chlorination can stem from adsorbed halo-organics on the porous electrode. However, as the adsorption is expected to decrease with the increase in the temperature, this is probably not the rate-determining step.

The de-chlorinations were performed on a porous iron electrode, under  $-1.5\ \text{V}$  for 5 h. Iron electrode ( $R=0.2\ \Omega$ ), Ar-saturated aqueous solutions containing  $\text{CH}_2\text{ClCH}(\text{OH})\text{COO}^-$ , 0.10 M  $\text{NaClO}_4$  at initial pH of 7,  $T=25^\circ\text{C}$ .

**Table 4**  
Reaction products of  $\text{CH}_2\text{BrCHBrCOO}^-$  de-bromination..

| E(V) | Acrylic acid, mM | Propionic acid, mM | $[\text{Acrylic acid}]/[\text{Propionic acid}]$ |
|------|------------------|--------------------|---|
| −1.5 | 1.4              | 7.5                | 0.2   |
| −0.5 | 4.7              | 0.15               | 31  |
| 0.0  | 2.6              | 0.070              | 37  |



### 3.3. De-halogenation of $\text{CH}_2\text{BrCHBrCOO}^-$ on a porous iron electrode under the application of an electrical bias

The effect of applying an electrical bias on a porous iron electrode on the de-bromination reaction of  $\text{CH}_2\text{BrCHBrCOO}^-$  was investigated. The results in Table 4 show that at a low biased potentials acrylic acid is the major product, while at significant negative biased potentials propionic acid and some acrylic acid are the major products (with traces of lactic and glyceric acids), Table 4. (It should be noted that as considerable de-bromination occurs on  $\text{Fe}^0$  powders, Fig. 1 and Table 1, on the same time-scale, some of the products obtained might be clearly due to this reaction). These results indicate that the mechanism of the  $\text{CH}_2\text{BrCHBrCOO}^-$  de-bromination on the iron surface is changed by applying an external electrical bias that also protects the metal surface from corrosion. The application of negative voltages to the porous iron electrode accelerates the de-halogenation reaction and modifies the decomposition mechanism of the Fe-C  $\sigma$  bond. The proposed mechanism for the de-bromination of this system is presented in Scheme 2.

The de-brominations were performed on a porous iron electrode, under different applied potentials for 4 h. Porous iron electrode ( $R=0.2\ \Omega$ ), Ar-saturated aqueous solutions containing  $0.010\ \text{M}\ \text{CH}_2\text{BrCHBrCOO}^-$ ,  $0.10\ \text{M}\ \text{NaClO}_4$  at initial pH of 3,  $T=25\ ^\circ\text{C}$ .

It should be noted that when the two substrates,  $\text{CH}_2\text{BrCHBrCOO}^-$  and  $\text{CH}_2\text{ClCH(OH)COO}^-$ , are de-halogenated, the same overall products are generated, but at different relative yields. The differences in the decomposition mechanisms of  $(\text{Fe}^0)^{2+}\text{-CH}_2\text{CH(OH)CO}_2^-$  (Scheme 3) and  $(\text{Fe}^0)^{2+}\text{-CH}_2\text{CHBrCO}_2^-$  (Scheme 2) may be related to the fact that elimination of  $\text{OH}^-$  is more difficult than  $\text{Br}^-$  elimination. Another possibility is that the main intermediate in the  $\text{CH}_2\text{BrCHBrCO}_2^-$  system is  $\text{Fe}^{2+}\text{-CH}(\text{CH}_2\text{Br})\text{CO}_2^-$ .

The results obtained in this study are in accord with earlier reports that the first step in the de-halogenation of organic compounds by ZVI is the formation of an alkyl radical and the halide anion. The radical reacts with the surface of the ZVI forming transients of the type  $(\text{Fe}^0)^{2+}\text{-CR}^1\text{R}^2\text{R}^3$ . The mechanism of decomposition of the latter transients depends on the nature of the substituents  $\text{R}^i$ , on the pH, the temperature, etc.

## 4. Concluding remarks

The application of an electrical voltage bias on the ZVI dramatically changes the mechanism of decomposition of the  $(\text{Fe}^0)^{2+}\text{-CR}^1\text{R}^2\text{R}^3$  transients. The most dramatic effect is in the heterolysis of  $(\text{Fe}^0)^{2+}\text{-CH}_2\text{CH(OH)CO}_2^-$  that at 0 V bias yields lactic and acrylic acid whereas glyceric acid is formed when a significant negative potential bias is applied. This means that the polarity of the Fe-C  $\sigma$  bond is reversed. Furthermore, the negative potential bias inhibits the passivation of ZVI and thus accelerates the de-halogenation process. Thus, the results suggest that in batch de-halogenation of pollutants the application of negative potential biases is desired.

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